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(54)【発明の名称】 発泡性熱可塑性樹脂粒子の製造法

(57)【要約】

【構成】 熱可塑性樹脂(A)、例えばポリスチレンと、発泡剤(B)、例えばブタンと、該熱可塑性樹脂(A)100重量部に対して1.5重量部以下の無機質粉末(C)、例えばタルクとを溶融混練し、次いでこれをダイヘッドの押出孔から加圧液中に押出し、即時切断した後、冷却する。

【効果】 発泡剤が熱可塑性樹脂中に容易に分散するため、内部発泡によるボイドの発生、粒子表面からの発泡剤の逸散、粒子内部への水分を巻き込み等がなく、均一な発泡ができ、良好な予備発泡粒子や発泡成形品が安定して得られる発泡性熱可塑性樹脂粒子を容易に製造できる。

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## 【特許請求の範囲】

【請求項1】 熟可塑性樹脂(A)と、発泡剤(B)と、該熟可塑性樹脂(A)100重量部に対して1.5重量部以下の無機質粉末(C)とを溶融混練し、次いでこれをダイヘッドの押出孔から加圧液中に押し出し、即時切断した後、冷却することを特徴とする発泡性熟可塑性樹脂粒子の製造法。

【請求項2】 熟可塑性樹脂(A)が芳香族ビニル系樹脂であり、かつ発泡剤(B)が常温常圧下で気体となるものである請求項1記載の製造法。

【請求項3】 熟可塑性樹脂(A)がステレン系樹脂であり、かつ発泡剤(B)が大気圧下での沸点が95℃以下ものである請求項1記載の製造法。

【請求項4】 無機質粉末(C)の使用量が、熟可塑性樹脂(A)100重量部に対して0.005~1.0重量部である請求項2又は3記載の製造法。

【請求項5】 熟可塑性樹脂(A)と、発泡剤(B)と、無機質粉末(C)とを溶融混練し、次いでこれをダイヘッドの押出孔から発泡性熟可塑性樹脂粒子のガラス転移温度(以下、Tgと略す)+5℃以上の加熱加圧液中に押し出し、即時切断して得た粒子を、加熱加圧液中で徐冷するか、又は同温度以上に保持した後、冷却する請求項1~4のいずれか1つに記載の製造法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、発泡性熟可塑性樹脂粒子の製造法、詳細には熟可塑性樹脂と発泡剤と特定量の無機質粉末とを用いた溶融押出法による発泡性熟可塑性樹脂粒子の製造法に関する。

## 【0002】

【従来の技術】 従来、発泡性熟可塑性樹脂粒子、例えば発泡性ステレン系樹脂粒子の製造法としては、ステレン系樹脂の懸濁重合中あるいは重合後に発泡剤を混合し含浸させる懸濁重合法が一般的であるが、この製造法では粒度の均一のものが得られず、あるいは分離等による粒度調整が不可欠である。また、顔料等の着色剤による着色粒子の製造も制約が多く、ほとんど実施されていない。更に、この方法では廃品の発泡性熟可塑性樹脂粒子への再生が不可能であるという課題もある。

【0003】 発泡性熟可塑性樹脂粒子製造の別法として、ステレン系樹脂等の熟可塑性樹脂と発泡剤と無機質粉末とを押出機中で溶融混練し、ダイスの出口から加圧水中に押し出した後、粒子状に切断する溶融押出造粒法

(特公昭42-24072号公報)が知られており、この方法は、粒度調整、粒子の着色および廃品の再生が容易であるほか、無機質粉末の添加により押出工程でのスリップが防止でき、しかも発泡セルが比較的均一で、外観も改良された発泡性発泡性熟可塑性樹脂粒子が得られるという利点がある。

## 【0004】

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【発明が解決しようとする課題】 しかしながら、上記特公昭42-24072号公報には、実施例において無機質粉末を熟可塑性樹脂100重量部に対して2重量部と多量に使用しているため、ダイス孔より加圧水中に押し出されて切断された粒子は、粒子内に内部発泡によるボイドが発生し、粒子表面より発泡剤が逸散するとともに、粒子内部に水分を巻き込みやすくなる。このため、発泡成形品においても、発泡倍率の低下、含水率の増大を招き、強度も悪化してしまう危険性がある。

## 【0005】

【課題を解決するための手段】 本発明者等は、この様な状況を解決するため、鋭意検討した結果、無機質粉末を特定量以下の使用割合で添加すると、発泡剤が熟可塑性樹脂中に容易に分散するため、内部発泡によるボイドの発生、粒子表面からの発泡剤の逸散、粒子内部への水分を巻き込み等がなく、均一な発泡ができ、良好な予備発泡粒子や発泡成形品が安定して得られる発泡性熟可塑性樹脂粒子を容易に製造できることを見い出し、本発明を完成するに至った。

## 【0006】

即ち、本発明は、熟可塑性樹脂(A)と、

発泡剤(B)と、該熟可塑性樹脂(A)100重量部に

に対して1.5重量部以下の無機質粉末(C)とを溶融混練し、次いでこれをダイヘッドの押出孔から加圧液中に

押し出し、即時切断した後、冷却することを特徴とする発泡性熟可塑性樹脂粒子の製造法を提供するものである。

## 【0007】

本発明で用いる熟可塑性樹脂(A)としては、

発泡剤により発泡可能な樹脂であればよく、例えば

ポリスチレン、ステレン-ブタジエン共重合体(耐衝撃性ポリスチレン)、ステレン-(メタ)アクリル酸共重

## 合体、ステレン-無水マレイン酸共重合体、AS樹脂、

ABS樹脂等の芳香族ビニル系樹脂、塩化ビニル樹脂、

塩化ビニリデン樹脂、塩化ビニル-酢酸ビニル共重合体

等の塩化ビニル系樹脂、ポリエチレン、ポリプロピレン

等のオレフィン系樹脂、ポリ(メタ)アクリル酸メチル、

ポリ(メタ)アクリル酸エチル、メタクリル酸メチル

スチレン共重合体等のアクリル系樹脂、ポリエチ

レンテレフタート、ポリブチレンテレフタート等のポ

リエステル系樹脂、ポリカブロラクタム、ヘキサメチ

レンアジポアミド樹脂等のアミド系樹脂、ポリウレタン、

## 40 ポリカーボネート、ポリエーテルイミド、ポリフェニ

レンエーテル等の単独あるいは混合物が挙げられ、なかで

も芳香族ビニル系樹脂、オレフィン系樹脂が好ましく、

特にステレン系樹脂が好ましい。

## 【0008】

本発明で用いる発泡剤(B)としては、例

えば脂肪族炭化水素系発泡剤、ハロゲン化炭化水素系発

泡剤等が挙げられ、通常大気圧下での沸点が95℃以下

のものを用いる。

## 【0009】

上記脂肪族炭化水素系発泡剤としては、例

えばエタン、プロパン、プロピレン、ノルマルブタン、

## 50 イソブタン、イソブチレン、ノルマルベンタン、イソベ

ンタン、ネオペンタン、シクロペンタン、ヘキサン、石油エーテル等が挙げられ、またハロゲン化炭化水素系発泡剤としては、例えば塩化メチル、塩化エチル、ジクロロエタン、クロロホルム、フルオロメタン、ジフルオロメタン、トリフルオロメタン、ジフルオロエタン、トリフルオロエタン、フルオロクロロメタン、フルオロクロロエタン、ジクロロジフルオロメタン等が挙げられる。なかでも炭素原子数3~6の脂肪族炭化水素、特にノルマルブタン、イソブタン、イソブチレン、ノルマルベンタン、イソベンタンが好ましい。

【0010】発泡剤(B)の使用量は、熱可塑性樹脂(A)100重量部に対して、通常40重量部以下であり、なかでも粒子の凝集がなく、均一なセル径が得られる点で2~10重量部が好ましい。

【0011】本発明で用いる無機質粉末(C)としては、タルク、珪藻土、焼成パーライト、ペントナイト、陶土、アスペスト、ガラス、石灰石、酸化アルミニウム、炭酸マグネシウム、炭酸第二鉄等が挙げられ、これらは併用しても差し支えない。

【0012】また、無機質粉末(C)の添加量としては、熱可塑性樹脂(A)100重量部に対して1.5重量部以下であることが必須であり、なかでも0.005~1.0重量部が好ましい。該添加量が1.5重量部より多い場合には、得られる発泡性粒子内に内部発泡によるボイドが発生し、粒子表面より発泡剤が逸散とともに、粒子内部に水分を巻き込みやすくなる。

【0013】本発明の製造法において、熱可塑性樹脂(A)と発泡剤(B)と無機質粉末(C)とを溶融混練する方法としては、特に限定ではなく、例えば該(A)、(B)及び(C)の3成分を溶融混練機を用いて(A)の溶融温度以上で溶融混練する方法が挙げられる。通常は単軸押出機、二軸押出機、タンデム型押出機等の押出機を用い、該(A)、(B)及び(C)の3成分を溶融混練した後、これをダイヘッドの押出孔から押し出す方法が一般的であるが、なかでも発泡剤(B)及び無機質粉末(C)の分散が良好な点で二軸押出機やタンデム型押出機を用いると好ましい。また、発泡剤(C)は熱可塑性樹脂(A)が半溶融ないし溶融しているところ、例えば押出機の途中の部分から圧入すると好ましい。

【0014】この様に溶融混練された発泡剤含有熱可塑性樹脂は、通常溶融混練機の先に取り付けられたダイヘッドの押出孔から、加圧液中に押し出した後、即時切断して粒子とする。

【0015】ここで用いるダイヘッドとしては、例えば直径0.3~3mm、好ましくは0.5~1mmの押出孔を有するもの等が挙げられ、また切断装置としては、押出孔から押し出された発泡剤含有熱可塑性樹脂を即時高温状態で切断するカッターと加圧液とを内部に有するカッターチャンバーとが取付けられているものが挙げられる。

【0016】加圧液としては、上記粒子の発泡を防止可能な圧力以上に加圧した水、グリコール、エチレングリコール、水とエチレングリコールの混合物等が挙げられ、通常加熱加圧された水を用いる。

【0017】加圧液に加えられる圧力は、通常加圧液の温度における発泡剤の飽和蒸気圧以上の圧力であり、カッターチャンバーに加圧液を満たした場合で通常5kg/cm<sup>2</sup>以上、好ましくは10~20kg/cm<sup>2</sup>である。

10 【0018】加圧液の温度は、特に限定されず、常温でもよいが、切断して得られた発泡性熱可塑性樹脂粒子のガラス転移温度(以下、T<sub>g</sub>と略す)以上、特にT<sub>g</sub>から加圧下での加圧液の沸点未満の間の温度であると、得られた粒子が常温にまで急冷されないため、粒子内の残留応力が緩和されて、より均一な発泡ができる粒子が得られる様になり、好ましい。水を用いた場合の温度は、通常40~105°Cであり、なかでもスチレン系樹脂の場合の温度は、60~85°Cが好ましい。

【0019】次いで粒子は、大気圧下でも発泡しなくなる温度まで冷却してもよいが、直ちに冷却せずに加圧液の中でT<sub>g</sub>以上の温度に、通常2分間以上、好ましくは4~10分間保持(必要に応じてT<sub>g</sub>以上の温度内で温度を上昇又は低下させてもよい。)あるいはT<sub>g</sub>前後の温度、好ましくはT<sub>g</sub>±5度の温度範囲で徐冷して該粒子内の残留応力の緩和を更に進めた後、冷却、好ましくは平均毎分5°C以上の速度で急冷すると好ましい。冷却された粒子は、次いで常圧下で分離、乾燥される。

【0020】上記造粒後の粒子内の残留応力を緩和する方法は、特に限定されないが、例えばカッターチャンバーから出た発泡剤含有熱可塑性樹脂粒子を、加圧液と共に応力緩和用加圧容器にその上部から供給し、T<sub>g</sub>+5°C以上の温度以上に保持したまま、あるいはT<sub>g</sub>前後の温度、好ましくはT<sub>g</sub>±5度の温度範囲で徐冷しつつ加圧液中をゆっくり落下させて、粒子内の残留応力を緩和させ、該容器の底部から順次抜き出す方法、カッターチャンバーから出た発泡剤含有熱可塑性樹脂粒子を、加圧液と共に移送管、例えば螺旋状の移送管に流入させ、この管内をT<sub>g</sub>+5°C以上の温度以上に保持したまま、あるいはT<sub>g</sub>前後の温度、好ましくはT<sub>g</sub>±5度の温度範囲で徐冷しつつ加圧液と共に移送させて、粒子内の残留応力を緩和させる方法等が挙げられる。

【0021】また、粒子の冷却方法は、粒子の発泡を防止しつつ冷却できる方法であればよく、例えば加圧下、該粒子と加圧液、又は加圧液を分離した粒子に冷却液を混合して冷却する方法等が挙げられる。

【0022】

【実施例】以下に実施例および比較例を挙げて、本発明を更に詳細に説明するが、本発明はこれにより限定されるものではない。尚、例中の部および%は重量基準である。

## 【0023】実施例1

ポリスチレン100部とタルク0.02部とからなる混合物を第1段押出機と第2段押出機とからなるタンデム型押出機のホッパーより供給して押し出し、次いでブタン7部を第一段押出機後半の注入口より供給し、第1段押出機および第2段押出機でポリスチレンとブタンとを溶融混練した。この時、樹脂温度は200℃、樹脂圧力は110kg/cm<sup>2</sup>を示した。

【0024】溶融混練した樹脂を、第二段押出機のダイヘッド（押出孔0.7mmφ×100個）を通して、80℃、10kg/cm<sup>2</sup>の加圧水で満たされたカッターチャンバーの中に80kg/hrの割合で押し出し、直ちにカッターで水中カットして、0.9mm径の粒子を得た。

【0025】この粒子を6m<sup>3</sup>/hrの加圧水が循環し、80℃、10Kg/cm<sup>2</sup>に保持された500リットルの応力緩和用加圧容器中に移送し、5分間滞留させて粒子の残留応力を緩和させた後、冷却用加圧容器に移送して25℃まで冷却し、減圧後、粒子を系外へ取り出し、遠心脱水機で脱水し、乾燥して、発泡性ポリスチレン粒子の原粒を得た。

【0026】こうして得られた粒子のブタン含有量は5.5重量部であり、残留応力も少なく、粒子の含水率も0.01%と低く、予備発泡することにより70cc/gまで発泡し、発泡粒子のセル径も150～200μmと均一であった。

【0027】この発泡性ポリスチレン粒子の組成と製造条件と性状を表1に示す。尚、性状は以下の方法で測定又は評価した。

・粒子の含水率：トルエンに発泡性ポリスチレン粒子5重量部を溶かし、カールフィッシャー水分計により測定した。

・粒子の発泡剤含有量：ガスクロマトグラフィーにて測定した。

・粒子の平均粒子径：100個の発泡性ポリスチレン粒子の粒子径をダイヤルゲージで測定し、その平均値を求めた。

・粒子の残留応力：発泡性ポリスチレン粒子の表面を50倍の超音波顕微鏡写真にとり、その表面の縞模様の程度から目視にて残留応力の多少を判定評価した。

・粒子のTg：示差熱分析装置（DSC）にて測定した。

・発泡倍率（1/嵩密度）：ゲージ圧1kg/cm<sup>2</sup>のシステムで30秒間加熱して発泡させた発泡粒子の嵩密度を求め、その逆数として算出した。

・発泡粒子のセル径：上記と同様に発泡させた発泡

粒子10個の切断面を50倍の実体顕微鏡写真にとり、そのセルの径を測定し、範囲を求めた。

・発泡粒子セルの均一性：上記と同様にして50倍の実体顕微鏡写真にとり、セルの均一性を目視にて判定評価した。

・成形品外観：目視により判定した。

【0028】◎：優れている。

○：良好。

△：あまり良くない。

【0029】×：不良。

## 比較例1

押出機のホッパーより、ポリスチレンのみを供給し、タルクを用いずに押し出した以外は実施例1と同様にして、発泡性ポリスチレン粒子を得た。

【0030】こうして得られた粒子は、粒子内のブタンの微分散性が悪く、予備発泡することにより65cc/gまで発泡したが、発泡粒子のセル径は100～300μmとやや不均一であった。

【0031】この発泡性ポリスチレン粒子の組成と製造条件と性状を表1に示す。

## 比較例2

タルクの使用量を2.0部に変更した以外は実施例1と同様にして、発泡性ポリスチレン粒子を得た。

【0032】こうして得られた粒子の発泡粒子のセル径は100～250μmと比較例1よりも均一化し、成形品外観も良化したが、実施例1と比較すると、粒子の含水量が多く、発泡倍率、セル径の均一性、成形品外観において見劣りする結果となった。また、粒子自体に多数の気泡があり、内部発泡を起こしているもの多かつた。

【0033】この発泡性ポリスチレン粒子の組成と製造条件と性状を表1に示す。

## 比較例3

タルクの使用量を3.0部に変更した以外は実施例1と同様にして、発泡性ポリスチレン粒子を得た。

【0034】こうして得られた粒子は、粒子がやや発泡しており、粒子の含水量が2.0部と非常に多く、発泡剤の含有量は4.0部で、発泡倍率も50cc/gまでしか上がらなかった。また、発泡粒子のセル径は40～300μmと非常に不均一なものであり、成形品外観も悪いものしか得られなかった。

【0035】この発泡性ポリスチレン粒子の組成と製造条件と性状を表1に示す。

【0036】

【表1】

項目		実施例1	比較例1	比較例2	比較例3
組成	ポリスチレン (部)	100	100	100	100
	ブタン (部)	7	7	7	7
	タルク (部)	0.02	—	2.0	3.0
製造条件	押出機	タンデム型	タンデム型	タンデム型	タンデム型
	樹脂温度 (℃)	200	200	200	200
	ダイス樹脂圧力 (kg/cm <sup>2</sup> )	110	110	110	110
	押出量 (kg/hr)	80	80	80	80
	ダイスノズル孔径 (mm)	0.7	0.7	0.7	0.7
	ダイスノズル孔数 (個)	100	100	100	100
条件	加圧水温度 (℃)	80	80	80	80
	加熱加圧水圧力 (kg/cm <sup>2</sup> )	10	10	10	10
	容器内応力緩和時間 (分)	5	5	5	5
粒子の性状	粒子の含水率 (部)	0.01	0.01	0.1	2.0
	粒子の発泡剤含有量 (部)	5.5	5.5	5.0	4.0
	粒子の平均粒子径 (mm)	0.9	0.9	0.9	0.9
	粒子の残留応力	少	中	少	中
	粒子のTg (℃)	65	65	68	68
	発泡倍率 (1/密度) (cc/g)	70	65	67	50
	発泡粒子のセル径 (μm)	150~200	100~300	100~250	40~300
	発泡粒子セルの均一性	均一	不均一	不均一	不均一
	成形品の外観	○	△	○~△	×

【0037】実施例2~4

その性状をまとめて表3に示す。

表2に示す組成と製造条件で行なった以外は実施例1と 30 【0038】

同様にして各種の発泡性熱可塑性樹脂粒子を製造した。

【表2】

項 目		実施例2	実施例3	実施例4
組成	ポリスチレン (部)	100	-	-
	耐衝撃性ポリスチレン (部)	-	100	-
	SMAA *1) (部)	-	-	100
	ブタン (部)	7	8	4
	ベンタン (部)	-	-	2
	タルク (部)	0.3	-	-
	炭酸マグネシウム (部)	-	0.02	-
製造	珪藻土 (部)	-	-	0.05
	押出機	タンデム型	タンデム型	二軸
	樹脂温度 (℃)	200	200	180
	ダイス内樹脂圧力 (kg/cm <sup>2</sup> )	105	100	130
	押出量 (kg/hr)	70	90	100
	ダイスノズル孔径 (mm)	0.5	0.7	0.8
	ダイスノズル孔数 (個)	150	100	70
条件	加熱加圧水温度 (℃)	80	70	90
	加熱加圧水圧力 (kg/cm <sup>2</sup> )	15	12	15
	容器内応力緩和時間 (分)	10	5	5

\*1) SMAA : スチレン-メタクリル酸共重合体

【0039】

\* \* 【表3】

項 目	実施例2	実施例3	実施例4
粒子の含水率 (部)	0.02	0.01	0.01
粒子の発泡剤含有量(ブタン) (部)	5.5	6.2	3.0
" (ベンタン) (部)	-	-	1.8
粒子の平均粒子径 (mm)	0.7	0.9	1.0
粒子の残留応力	少	少	少
粒子のTg (℃)	65	63	80
発泡倍率(1/嵩密度) (cc/g)	6.7	7.0	6.5
発泡粒子のセル径 (μm)	100~130	120~150	150~200
発泡粒子セルの均一性	均一	均一	均一
成形品の外観	◎	◎	◎

【0040】

【発明の効果】本発明の発泡性熱可塑性樹脂粒子の製法によれば、発泡剤が熱可塑性樹脂中に容易に分散するため、内部発泡によるボイドの発生、粒子表面からの発

40 泡剤の逸散、粒子内部への水分を巻き込み等がなく、均一な発泡ができ、良好な予備発泡粒子や発泡成形品が安定して得られる発泡性熱可塑性樹脂粒子を容易に製造できる。

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(54) [Title of the Invention]

**MANUFACTURING METHOD FOR FOAMABLE THERMOPLASTIC RESIN**

**PARTICLES**

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(57) [Abstract]

[Construction]

A thermoplastic resin (A), such as polystyrene, a foaming agent (B), such as butane, and inorganic powder (C), such as talc, whose parts by weight is 1.5 or lower with respect to 100 parts by weight of the thermoplastic resin (A), are diffused and kneaded, and then extruded from extruding holes of die head into pressurized liquid and instantaneously cut, and [the obtained particles] are cooled.

[Effect]:

Since the foaming agent is easily minutely-dispersed into the thermoplastic resin, generation of voids due to internal foaming, dissipation of the foaming agent from surfaces of particles and inclusion of moisture inside the particles will not occur, so uniform foaming can be realized, and foamable thermoplastic resin particles where excellent preliminary foamed particles and foamed molded articles can be stably obtained can be easily manufactured.

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## [Claims]

### [Claim 1]

A manufacturing method for foamable thermoplastic resin particles, wherein, a thermoplastic resin (A), a foaming agent (B) and inorganic powder (C) whose parts by weight is 1.5 or less with respect to 100 parts by weight of said thermoplastic resin (A) are diffused and kneaded, and extruded from extrusion holes of a die head into a pressurized liquid, and after the extruded material is instantaneously cut, the obtained particles are cooled.

### [Claim 2]

The manufacturing method according to Claim 1, wherein, the thermoplastic resin (A) is an aromatic vinyl resin and the foaming agent (B) is gas at room temperature under normal pressure.

### [Claim 3]

The manufacturing method according to Claim 1, wherein, the thermoplastic resin (A) is a styrene resin and a foaming agent (B) the boiling point of which at atmospheric pressure is 95 °C or lower.

### [Claim 4]

The manufacturing method according to Claim 2 or 3, wherein, the usage of the inorganic powder (C) is 0.005 to 1.0 parts by weight with respect to 100 parts by weight of the thermoplastic resin (A).

### [Claim 5]

The manufacturing method according to any one of Claims 1 to 4, wherein, the thermoplastic resin (A), the foaming agent (B) and the inorganic powder (C) are fused and kneaded, and extruded from the extrusion holes of the die head into a pressurized

liquid whose temperature is glass transition temperature (hereafter abbreviated as Tg) of the foaming thermoplastic resin particle + 5 °C or more, and particles obtained by instantaneous cut are gradually cooled in a heated & pressurized liquid or after the particles are maintained at said temperature or higher, the particles are cooled.

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### **[Detailed Explanation of Invention]**

[0001]

[Technical field of the invention]

The present invention relates to a manufacturing method for foamable thermoplastic resin particles; and in particular, to a manufacturing method for foamable thermoplastic resin particles by a diffusion extruding method using a thermoplastic resin, a foaming agent and a specific amount of inorganic powder.

[0002]

[Prior Art]

Conventionally, as a manufacturing method for foamable thermoplastic resin particles, such as foamable styrene resin particles, a suspension polymerization method where a foaming agent is mixed and then impregnated during or after the suspension & polymerization of the styrene resin is generally used. However, a uniform particle diameter cannot be obtained with this manufacturing method, and it is essential to adjust the particle size by screening. Moreover, manufacturing of colored particles by a coloring agent, such as pigments, also has many restrictions, and is hardly implemented. In addition, this method also has a problem such that it is impossible to reclaim waste products to foamable thermoplastic resin particles.

[0003]

As another method for manufacturing the foamable thermoplastic resin particles, a diffusion extruding granulation method where a thermoplastic resin, such as styrene resin, a foaming agent and inorganic powder are diffused and kneaded in an extruding machine, and after being extruded from the outlets of dies into the pressurized water, is cut to particles (Japanese Patent Publication Sho 42-24072) is known, with the advantage that particle size adjustment, coloring of particles and reclamation of wasted products are easy; a slip in the extruding process can be prevented according to the addition of inorganic powder; foamed cells are considerably uniform; and foamable thermoplastic resin particles with improved appearance can be obtained.

[0004]

[Problems to be Solved by Invention]

However, in the above Publication of Japanese Patent Publication Sho 42-24072, since a large amount of inorganic powder, 2 parts by weight with respect to 100 parts by weight of the thermoplastic resin, is used in examples, in particles that have been extruded from holes of dies into pressurized water and cut, voids due to internal foaming occur, the foaming agent dissipates from surfaces of the particles; concurrently, moisture is easily contained within the particles. Consequently, there is a risk of causing a decrease of the foaming ratio and an increase of moisture content, even in foamed molded articles, and the strength may also deteriorate.

[0005]

[Problem Resolution Means]

In order to solve these circumstances, as a result of close examination, the inventors of the present application discovered that when the inorganic powder is added at a use ratio of a specific amount or less, the foaming agent easily minutely-disperses into the thermoplastic resin, so generation of voids due to the internal foaming,

dissipation of the foaming agent from the surfaces of particles, and inclusion of moisture into the particles will not occur, and uniform foaming can be realized and foamable thermoplastic resin particles where excellent preliminary foamed particles and foamed molded articles can be easily manufactured, completing the present invention.

[0006]

In other words, the present invention is to provide a manufacturing method for foamable thermoplastic resin particles characterized such that the thermoplastic resin (A), the foaming agent (B) and the inorganic powder (C) whose content is 1.5 parts or less by weight with respect to 100 parts by weight of said thermoplastic resin (A) are diffused and kneaded; extruded from the extruding holes of the die head into a pressurized liquid; and after instantaneously being cut, is cooled.

[0007]

As the thermoplastic resin (A) used in the present invention, any resin is acceptable as long as it is foamable by a foaming agent, and for example, single substance or a compound of an aromatic vinyl resin, such as polystyrene, styrene, styrene-butadiene copolymer (impact-resistant polystyrene), styrene-(meta) acrylic acid copolymer, styrene-maleic acid anhydride copolymer, AS resin or ABS resin; a vinyl chloride resin, such as vinyl chloride resin, vinylidene chloride resin or vinyl chloride-vinyl acetate copolymer; an olefin resin, such as polyethylene or polypropylene; an acryl resin, such as poly (meta) methyl acrylate, poly (meta) ethyl acrylate or methyl methacrylate-styrene copolymer; a polyester resin, such as polyethylene terephthalate or polybutylene terephthalate; an amide resin, such as polycaprolactam or hexamethylene adipamide resin; polyurethane, polycarbonate,

polyetherimide or polyphenylen ether; can be cited, and among them, the aromatic vinyl resin and the olefin resin are preferable, and the styrene resin is especially preferable.

[0008]

As the foaming agent (B) used in the present invention, for example, an aliphatic hydrocarbon foaming agent and a halogenated hydrocarbon foaming agent can be cited, and normally, an agent whose boiling point is under the atmospheric pressure at 95 °C or lower is used.

[0009]

As the aliphatic hydrocarbon foaming agent, for example, ethane, propane, propylene, normal butane, isobutane, isobutylene, normal pentane, isopentane, neopentane, cyclopentane, hexane and petroleum ether can be cited; as the halogenated hydrocarbon foaming agent, for example, methyl chloride, ethyl chloride, dichloroethane, chloroform, fluoromethane, difluoromethane, trifluoromethane, difluoroethane, trifluoroethane, fluorochloromethane, fluorochloroethane and dichlorodifluoromethane can be cited. Among them, aliphatic hydrocarbon whose hydrocarbon number is 3 to 6, especially, normal butane, isobutane, isobutylene, normal pentane and isopentane are preferable.

[0010]

The usage of the foaming agent (B) is normally 40 parts by weight or less with respect to 100 parts by weight of the thermoplastic resin (A), and 2 to 10 parts by weight are preferable because of points to obtain uniform cell diameter without any agglomeration of particles.

[0011]

As the inorganic powder (C), talc, diatomaceous earth, calcined perlite, bentonite, porcelain clay, asbestos, glass, lime stone, aluminum oxide, magnesium carbonate and ferric carbonate can be cited, and there is no harm in using combination of these materials.

[0012]

Moreover, the additive amount of the inorganic powder (C) must be 1.5 parts by weight with respect to 100 parts by weight of the thermoplastic resin (A), and [the range of] 0.005 to 1.0 parts by weight is desirable. When said additive amount is greater than 1.5 parts by weight, voids due to the internal foaming occur within the foamable particles to be obtained, and the foaming agent dissipates from the surfaces of the particles; concurrently, it becomes easy to include moisture inside the particles.

[0013]

In the manufacturing method of the present invention, a method to diffuse and knead the thermoplastic resin (A), the foaming agent (B) and the inorganic powder (C) has no special limitation, and for example, a method to diffuse and knead the three components of (A), (B) and (C) using a diffusing & kneading machine at a diffusing temperature of (A) or higher can be cited. Normally, methods where, after said three components (A), (B) and (C) are diffused and kneaded using an extruder, such as a single screw extruder, a twin screw extruder or a tandem type extruder, the material is generally extruded from extruding holes of die head, among which it is preferable to use the twin screw extruder or the tandem type extruder because the dispersion of the foaming agent (B) and the inorganic powder (C) is excellent. Moreover, it is preferable that the foaming agent (C) be pressed into the material, for example, from a

portion of the middle of the extruder when the thermoplastic resin (A) is semi-diffused or diffused.

[0014]

After the thermoplastic resin containing the foaming agent diffused & kneaded as described above is normally extruded into a pressurized liquid from the extruding hole of the die head mounted at the end of the diffusing kneader, it is instantaneously cut, and particles are obtained.

[0015]

As the die head used herein, for example, one having extruding holes with 0.3 to 3 mm of diameter, preferably 0.5 to 1 mm, can be cited, and as a cutting device, one mounting a cutter to instantaneously cut the thermoplastic resin containing the foaming agent under a high temperature condition and a cutter chamber having a pressurized liquid inside can be cited.

[0016]

As the pressurized liquid, water, glycol, ethylene glycol or a mixture of water and ethylene glycol where pressure to enable the prevention of foaming of above particles or higher is applied can be cited, and heated & pressurized water is normally used.

[0017]

The pressure applied to the pressurized liquid is normally saturated vapor pressure of the foaming agent at the temperature of the pressurized liquid or higher, and when the pressurized liquid is filled in the cutter chamber, the pressure is normally 5 kg/cm<sup>2</sup>, preferably 10 to 20 kg/cm<sup>2</sup>.

[0018]

The temperature of the pressurized liquid is not particularly limited, and can be room temperature. However, if the temperature is higher than the glass transition temperature (hereafter, abbreviated as Tg) of the foamable thermoplastic resin particles obtained by cutting, especially between Tg and less than the boiling point of the pressurized liquid under increased pressure, because the obtained particles will not be rapidly quenched to room temperature, the residual stress within the particles is relaxed and the particles with more uniform foaming can be obtained, it is preferable. The temperature in the case of using water is normally 40 to 105 °C, and among them, for the temperature in the case of a styrene resin, the range of 60 through 85 °C is preferable.

[0019]

Next, the particles can be cooled to the temperature where the particles will not foam even under the atmospheric pressure. However, it is preferable that after the particles are retained in the pressurized liquid at Tg or higher for 2 minutes or longer, preferably 4 to 10 minutes (the temperature can be increased or lowered within the range of Tg or higher), without immediately cooling down, or after the particles are gradually cooled around Tg, preferably within the range of temperature range of Tg ± 5 °C, and the relaxation of residual stress within said particles is further in progress, the particles are cooled, preferably rapidly quenched at the rate of 5 °C or more per minute, isolated and dried at ordinary pressure.

[0020]

A method to relax the residual stress within the particles after the above granulation is not particularly limited, and for example, a method can be cited where the thermoplastic resin particles containing the foaming agent extracted from the cutter

chamber are supplied to a pressurized container for stress relaxation from the top along with the pressurized liquid, and while the particles are maintained at  $T_g + 5$  °C or higher, or gradually cooled at around  $T_g$ , preferably within the temperature range of  $T_g \pm 5$  °C, the particles are slowly dropped in the pressurized liquid, and then, the residual stress within the particles is relaxed and the particles are sequentially extracted from the bottom of said container, and another method where the thermoplastic resin particles containing the foaming agent extracted from the cutter chamber flow into a transfer tube, for example, a spiral transfer tube, along with the pressurized liquid, and while the inside of the tube is maintained at  $T_g + 5$  °C or higher, or gradually cooled at around  $T_g$ , preferably within the temperature range of  $T_g \pm 5$  °C, the particles are transferred along with the pressurized liquid, and the residual stress within the particles is relaxed.

[0021]

Moreover, for the cooling method for the particles, any method is acceptable as long as it is a method to cool down the particles while foaming of the particles is prevented, and for example, a method can be cited to cool down [the particles] by mixing a cooling liquid into said particles and the pressurized liquid, or the particles where the pressurized liquid is isolated.

[0022]

#### **[Examples]**

Hereafter, the present invention is described in further detail with reference to examples and comparative examples. However, the present invention shall not be limited to these examples. Furthermore, 'parts' and '%' in the examples are based upon weight.

[0023]

**Example 1:**

A mixture consisting of 100 parts of polystyrene and 0.02 parts of talc was supplied and extruded from a hopper of a tandem type extruder composed of a first stage extruder and a second stage extruder, and next, 7 parts of butane were supplied from an inlet of the latter side of the first stage extruder, and polystyrene and butane

were diffused and kneaded by the first stage extruder and the second stage extruder.

At this time, the resin temperature was 200 °C and the resin pressure was 110 kg/cm<sup>2</sup>.

[0024]

The diffused and kneaded resin was extruded into a cutter chamber filled with pressurized water, at 80 °C and 10 kg/cm<sup>2</sup>, at the rate of 80 kg/hr through a die head of the second stage extruder (extruding hole: 0.7 mm $\phi$  × 100 pieces), and [the material] was immediately cut in the water and particles with 0.9 mm of diameter were obtained.

[0025]

These particles were transferred into a 500-litter pressurized container for stress relaxation, where pressurized water was circulated at [the rate of] 6 m<sup>3</sup>/hr, and which was maintained at 80 °C and 10 kg/cm<sup>2</sup>, and after they were retained for 5 minutes and the residual stress of the particles was relaxed, these were transferred to the pressurized container for cooling and cooled to 25 °C, and after the pressure was reduced, the particles were extracted to the outside of the system, and they were dehydrated with a centrifugal dehydrator and dried, thereby obtaining crude particles of foamable polystyrene particles.

[0026]

The butane content in the obtained particles was 5.5 parts by weight; the residual stress was also small; the moisture content in the particles was also low, 0.01 %; preliminary foaming resulted in the foaming to 70 cc/g; and the cell diameter of the foamable particles was also uniform, 150 to 200  $\mu\text{m}$ .

[0027]

The composition, manufacturing conditions and properties of these foamable polystyrene particles are shown in Table 1. Furthermore, the properties were measured and evaluated with the following methods:

- Moisture content in particles: Five parts by weight of foamable polystyrene were dissolved in toluene, and the moisture content was measured by a Karl Fischer moisture meter.
- Content of foaming agent in particles: The content was measured by a gas chromatography.
- Average diameter of particles: Particle diameters of 100 foamable polystyrene particles were measured by a dial gauge, and an average value was calculated.
- Residual stress of particles: The surface of the foamable polystyrene particles was imaged by a 50X ultrasonic microscope, and the magnitude of the residual stress was visually determined and evaluated according to the degree of a striped pattern on the surface.
- $T_g$  of particles:  $T_g$  was measured by a differential scanning calorimeter (DSC).
- Foaming rate (1/bulk density): The bulk density of the foamable particles, which were foamed by heating with steam at 1  $\text{kg}/\text{cm}^2$  of gauge pressure for 30 seconds, was obtained, and its inverse number was calculated.

- Cell diameter of foamable particles: Cross sectional surfaces of 10 foamable particles, which were foamed similarly to the above, were imaged with a 50X stereoscopic microscope, and their cell diameters were measured and the range was obtained.
- Uniformity of foamable particle cells: [The cross sectional surfaces of 10 foamable particles] were imaged with a 50X stereoscopic microscope as similar to the above, and the cell uniformity was visually determined and evaluated.
- Appearance of molded articles: The appearance was visually determined.

[0028]

◎: excellent, ○: good, △: not good

[0029]

×: inadequate

#### **Comparative Example 1:**

Procedures similar to Example 1 were conducted except for supplying only polystyrene from a hopper of an extruder and extruding [the material] without using talc, thereby obtaining foamable polystyrene particles.

[0030]

With the particles obtained as cited above, differential dispersibility of butane within the particles was poor, and the preliminary foaming resulted in foaming up to 65 cc/g; however, the cell diameters of the foamable particles were slightly uneven, at 100 to 300  $\mu\text{m}$ .

[0031]

The composition, manufacturing conditions and properties of the foamable polystyrene particles are shown in Table 1.

**Comparative Example 2:**

With the similar procedures to those in Example 1 except for changing the usage of talc to 2.0 parts, foamable polystyrene particles were obtained.

[0032]

The cell diameters of the foamable particles described above were further made uniform, 100 to 250  $\mu\text{m}$ , compared to those in Comparative Example 1, and the appearance of the molded articles was also improved. However, compared to Example 1, the moisture content was greater, and the foaming rate, the uniformity of cell diameter and the appearance of molded articles were all inferior. Moreover, many bubbles were generated in the particles themselves, and there were many particles where the internal foaming occurred.

[0033]

The composition, manufacturing conditions and properties of these foamable polystyrene particles are shown in Table 1.

**Comparative Example 3:**

Foamable polystyrene particles were obtained with similar procedures to those of Example 1, except for changing the usage of talc to 3.0 parts.

[0034]

Particles obtained as described above were slightly foamed, and the moisture content in the particles was very high, at 2.0 parts. In the meantime, the content of the foaming agent was 4.0 parts, and the foaming rate increased only to 50 cc/g, as well. Moreover, the cell diameters of the foamable particles were not so uniform, at 40 to 300  $\mu\text{m}$ , and the appearance of the molded articles was perceived as being of poor quality.

[0035]

The composition, manufacturing conditions and properties of these foamable polystyrene particles are shown in Table 1.

[0036]

Table 1:

Item		Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3
Composition	Polystyrene (parts)	1 0 0	1 0 0	1 0 0	1 0 0
	Butane (parts)	7	7	7	7
	Talc (parts)	0. 0 2	—	2. 0	3. 0
Manufacturing conditions	Extruding machine	Tandem type	Tandem type	Tandem type	Tandem type
	Resin temperature (°C)	2 0 0	2 0 0	2 0 0	2 0 0
	Resin pressure of dies (kg/cm <sup>2</sup> )	1 1 0	1 1 0	1 1 0	1 1 0
	Extrusion output (kg/hr)	8 0	8 0	8 0	8 0
	Diameter of nozzle hole in dies (mm)	0. 7	0. 7	0. 7	0. 7
	Number of nozzle holes in dies (pieces)	1 0 0	1 0 0	1 0 0	1 0 0
	Temperature of pressurized water (°C)	8 0	8 0	8 0	8 0
	Pressure of heated & pressurized water (kg/cm <sup>2</sup> )	1 0	1 0	1 0	1 0
	Stress relaxation time within container (min)	5	5	5	5
Moisture content of particles (parts)		0. 0 1	0. 0 1	0. 1	2. 0
Foaming agent content in particles (parts)		5. 5	5. 5	5. 0	4. 0
Average particle diameter of particles (mm)		0. 9	0. 9	0. 9	0. 9
Remaining stress of particles		Less	Medium	Less	Medium
Tg of particle (°C)		6 5	6 5	6 8	6 8
Foaming ratio (1/ bulk density) (cc/g)		7 0	6 5	6 7	5 0
Cell diameters of foammable particles (μm)		150~200	100~300	100~250	40~300
Uniformity of foammable particle cells		Uniform	Slightly uniform	Slightly uniform	Not uniform
Appearance of molded articles		◎	△	○~△	×

[0037]

**Examples 2 to 4:**

Various foamable thermoplastic resin particles were manufactured in a manner similar to Example 1 except for compositions and manufacturing conditions shown in Table 2. Their properties are summarized in Table 3.

[0038]

Table 2:

Item		Example 2	Example 3	Example 4
Composition	Polystyrene (parts)	<b>1 0 0</b>	—	—
	Impact resistance polystyrene (parts)	—	<b>1 0 0</b>	—
	SMAA *1) (parts)	—	—	<b>1 0 0</b>
	Butane (parts)	<b>7</b>	<b>8</b>	<b>4</b>
	Pentane (parts)	—	—	<b>2</b>
	Talc (parts)	<b>0 . 3</b>	—	—
	Magnesium carbonate (parts)	—	<b>0 . 0 2</b>	—
	Diatom earth (parts)	—	—	<b>0 . 0 5</b>
Manufacturing conditions	Extruding machine	Tandem type	Tandem type	Twin screw type
	Resin temperature (°C)	<b>2 0 0</b>	<b>2 0 0</b>	<b>1 8 0</b>
	Resin pressure within dice (kg/cm <sup>2</sup> )	<b>1 0 5</b>	<b>1 0 0</b>	<b>1 3 0</b>
	Extrusion output (kg/hr)	<b>7 0</b>	<b>9 0</b>	<b>1 0 0</b>
	Diameter of dice nozzle hole (mm)	<b>0 . 5</b>	<b>0 . 7</b>	<b>0 . 8</b>
	Number of dice nozzle holes (pieces)	<b>1 5 0</b>	<b>1 0 0</b>	<b>7 0</b>
	Temperature of heated pressure-applied water (°C)	<b>8 0</b>	<b>7 0</b>	<b>9 0</b>
	Pressure of heated & pressure-applied water (kg/cm <sup>2</sup> )	<b>1 5</b>	<b>1 2</b>	<b>1 5</b>
Stress relaxation time within container (min)		<b>1 0</b>	<b>5</b>	<b>5</b>

\*1) SMAA: styrene-meta acrylic acid copolymer

[0039]

Table 3

Item		Example 2	Example 3	Example 4
Moisture content of particle	(parts)	<b>0.02</b>	<b>0.01</b>	<b>0.01</b>
Foaming agent content in particle (Butane)	(parts)	<b>5.5</b>	<b>6.2</b>	<b>3.0</b>
Foaming agent content in particle (Pentane)	(parts)	—	—	1.8
Average particle diameter of particles	(mm)	<b>0.7</b>	<b>0.9</b>	<b>1.0</b>
Remaining stress of particles		Less	Less	Less
Tg of particles	(°C)	<b>65</b>	<b>63</b>	<b>80</b>
Forming ratio (1/bulk density)	(cc/g)	<b>6.7</b>	<b>7.0</b>	<b>6.5</b>
Cell diameter of foamable particles	(μm)	<b>100~130</b>	<b>120~150</b>	<b>150~200</b>
Uniformity of foamable particle cells		Uniform	Uniform	Uniform
Appearance of molded articles		◎	◎	◎

[0040]

#### [Effect of the Invention]

According to the manufacturing method for foamable thermoplastic resin particles of the present invention, since a foaming agent is easily minutely-dispersed into the thermoplastic resin, no void due to internal foaming, no dissipation of the foaming agent from the particle surface and no inclusion of moisture inside the particles are observed, so uniform foaming can be realized, and foamable thermoplastic resin particles where excellent preliminarily-foamed particles and foamed molded articles can be stably obtained can be easily manufactured.